Influencing the "Injection Barriers" into Prototype Molecular Wires through Metal-molecule Coupling

NIST is developing new metrology tools that provide the research and industrial communities with the metrology capabilities for electrical conduction characteristics of molecular species either as organic electronic devices or molecular electronic devices of the future. The drive to introduce organic molecular materials into electronic device applications, (organic electronics) is motivated by a number of potentially attractive features, such as ease of fabrication, ability to fabricate on flexible substrates, and the wide extent to which organic materials can be functionalized via organic synthetic methods. A range of applications is foreseen for organic field effect transistors and light emitting diodes including, for instance, flexible displays and other low cost flexible electronics.

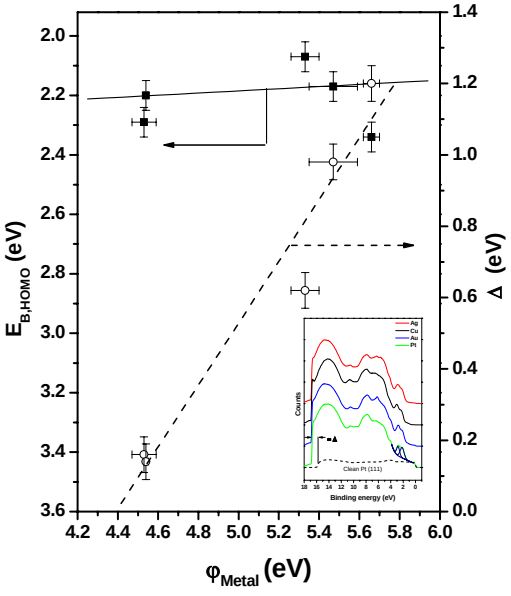
R.D. Van Zee and C.D Zangmeister (Div. 836)

In addition to replacing inorganic semiconductors in more or less conventional device architectures, organic systems are also of interest in the more speculative, and potentially more revolutionary, area of "molecular electronics". Here, it is envisioned that the nonlinear characteristics of individual molecules, or small ensembles, will provide the required device functionality, allowing low cost chemical synthetic methods to replace, at least partially, multi-billion dollar semiconductor fabrication lines in the production of nanoscale device structures.

In either application format, charge injection at a molecule-contact interface plays a vital role in controlling transport and, thus, potential device performance. Interfacial charge injection is dictated by chemical bonding and the resulting band line-up between the Fermi level of the contact and transport levels of the molecule. Information relating to band line-up is difficult to obtain using conventional techniques in the case of the single-molecule length-scale systems of interest in molecular electronics. We have employed a combination of one-photon (He I resonance excitation) and two-photon photoelectron spectroscopy, using sub-picosecond Ti:sapphire laser-based excitation, to determine the electronic structure, including injection barriers to both occupied and unoccupied levels on a variety of self-assembled monolayers.

The majority of studies of covalently bound monolayers on metallic surfaces involve thiol-coupling (R-SH) chemistry. Self-assembly of monolayers utilizing thiol chemistry is known to form robust, reproducible monolayers on a variety of metallic surfaces. Prototypical thiol-bound molecular systems have been previously studied on poly- and single crystal gold surfaces. To date charge injection barriers of thiol-bound systems on other metals have yet to be determined. This data is fundamental to develop future devices and standards of molecular-based systems. We have undertaken a study of thiol-bound monolayers on a variety of single crystal metallic surfaces (Ag, Cu, Au, Pt). This data allows us to determine two important factors governing behavior in future devices. First, we gain an understanding in how injection barriers vary on a variety of metal surfaces and how the molecular structure effects the alignment of the molecular orbitals with the metal electronic structure. Second, this allows us to develop models and relationships of how the molecular orbiatals of thiol-bound, and other linking chemistries, are aligned to metal surfaces. From these data we can draw important links and analogous behavior between molecular electronics and semiconductors-based devices.

The NIST work adds important insights to the factors that influence band alignment at metal-organic interfaces, a parameter that plays a critical role in potential applications of organic materials in emerging electronic technologies.



Band alignment parameters of a thiol-bound model molecular wire monolayer on several metal surfaces. One photon photoemission spectra are shown in the figure.

Future Plans: We aim to build upon our previous studies of understanding the affect molecular structure and metal have on controlling band line-up in covalently bound molecular systems. Our future work will look into other linking-chemistries on a variety of metal and semiconducting surfaces.